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NATIONAL INVENTORY OF SOURCES AND EMISSIONS: VANADIUM -1968

W. E. Davis and Associates

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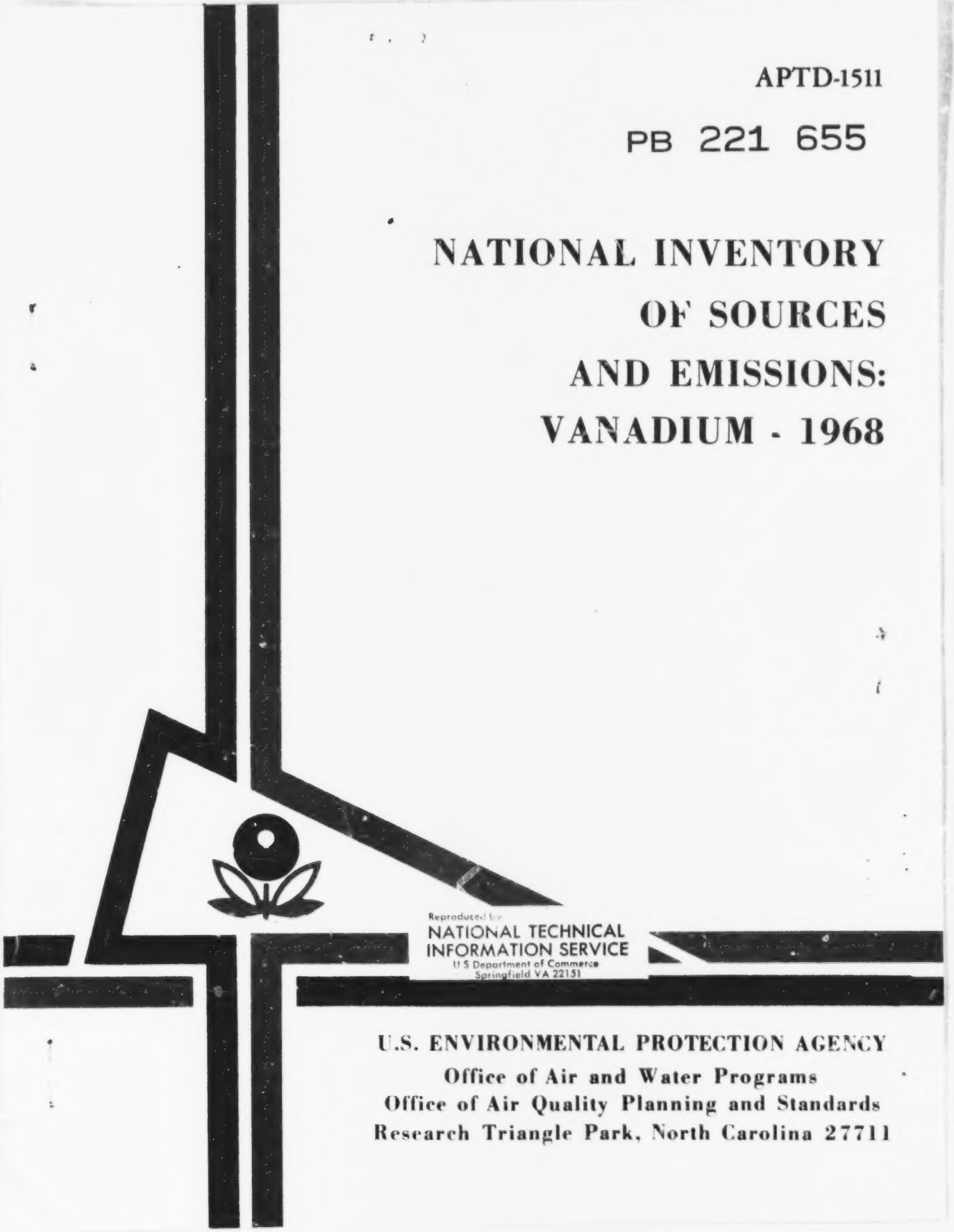

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NATIONAL INVENTORY OF SOURCES AND EMISSIONS: VANADIUM - 1968

by

W. E. Davis & Associates
9726 Sagamore Road
Leawood, Kansas

Contract No. CPA-70-128

EPA Project Officer: C. V. Spangler

Prepared for

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Office of Air and Water Programs
Office of Air Quality Planning and Standards
Research Triangle Park, N.C. 27711

June 1971

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Publication No. APTD-1511

PREFACE

This report was prepared by W. E. Davis & Associates pursuant to Contract No. CPA 70-128 with the Environmental Protection Agency, Office of Air Programs.

This inventory of atmospheric emissions has been prepared to provide reliable information regarding the nature, magnitude, and extent of the emissions of vanadium in the United States for the year 1968.

Background information concerning the basic characteristics of the vanadium industry has been assembled and included. Process descriptions are given, but they are brief, and are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant.

Due to the limitation of time and funds allotted for the study, the plan was to personally contact about thirty percent of the companies in each major emission source group to obtain the required information. It was known that published data concerning emissions of the pollutant was virtually nonexistent, and contacts with industry ascertained that atmospheric emissions were not a matter of record.

The vanadium emissions and emission factors presented are based on the summation of information obtained from production and reprocessing companies that handle about twenty-five percent of the vanadium consumed in the United States. Vanadium emissions and emission factors are considered to be reasonably accurate.

ACKNOWLEDGEMENTS

This was an industry oriented study and the authors express their appreciation to the many companies and individuals in the vanadium industry for their contributions.

We wish to express our gratitude for the assistance of the various societies and associations, and to many branches of the Federal and State Governments.

Our express thanks to Mr. C. V. Spangler, Project Officer, Office of Air Programs, for his helpful guidance.

CONTENTS

SUMMARY 1

Emissions by Source 2
Emissions by States 3
Emission Factors 4

SOURCES OF VANADIUM 5

MATERIAL FLOW

Material Flow Chart 7
Mining and Processing 8
Imports and Exports 9
Vanadium Stocks 10
Reprocessing 11
Carbon Steel 11
Alloy Steel 12
Cast Iron 13
Nonferrous Alloys 14
Chemicals and Ceramics 16
Miscellaneous 18

EMISSIONS

Mining and Processing 21
Metallurgical Processing 23
Reprocessing 29
Steel 30
Cast Iron 36
Nonferrous Alloys 37
Chemicals and Ceramics 37
Miscellaneous 39
Consumptive Uses 41
Coal 41
Oil 44

APPENDIX A

Companies Dealing in Vanadium and Vanadium Products 50

TABLES

Table I
Average Minor Element Contents of Coals from Various Regions of the United States - ppm 43
Table II
Vanadium Content of Domestic Crude Oils . . 45
Table III
Vanadium Content of Venezuelan Crude Oils 46
Table IV
Vanadium Content of Middle East Crude Oils 48

SUMMARY

The production and use of vanadium in the United States has been traced and charted for the year 1968. The consumption was 5,495 tons, exports 741 tons, and imports 652 tons. About 80 percent (4,350 tons) was used in the production of steel.

Emissions to the atmosphere during the year totaled 19,231 tons. Emissions due to the combustion of fuel oil and coal were 17,000 tons and 1,750 tons, respectively. Emissions resulting from the production of ferrovanadium were 144 tons and those from the production of steel were 236 tons.

Emission estimates for coal and fuel oil combustion are considered to be reasonably accurate. They are based on the average vanadium content of many coal and oil samples.

EMISSIONS BY SOURCE
1968

Source Category	Source Group		Short Tons
Mining and Processing			81
Metallurgical Processing			144
Reprocessing			244
	Steel		
	Blast Furnace	63	
	Open-Hearth Furnace	166	
	Basic Oxygen Furnace	7	
	Electric Arc Furnace	N	
	Cast Iron	1	
	Nonferrous Alloys	3	
	Chemicals and Ceramics		
	Catalysts	2	
	Glass and Ceramics	N	
	Miscellaneous	2	
Consumptive Uses			18,750
	Coal	1,750	
	Oil	17,000	
	TOTAL		19,219

N - Negligible (less than 1 ton)

EMISSIONS BY STATES
1968

State	Short Tons
New York	3,460
California	1,880
Massachusetts	1,740
New Jersey	1,730
Pennsylvania	1,400
Georgia and Florida	1,290
Illinois	760
Connecticut	720
Delaware and Maryland	470
Indiana	430
Virginia	420
Ohio	360
All Other States	4,090
Undistributed	469
TOTAL	19,219

EMISSION FACTORS

Mining and Processing	25 lb/ton of vanadium processed
Metallurgical Processing	61 lb/ton of vanadium processed
Reprocessing	
Steel	
Blast Furnace	1.4 lb/1,000 tons of pig iron produced
Open-Hearth Furnace	5.1 lb/1,000 tons of steel produced
Basic Oxygen Furnace	0.3 lb/1,000 tons of steel produced
Cast Iron	0.22 lb/ton of charge
Nonferrous Alloys	12 lb/ton of vanadium processed
Chemicals and Ceramics	
Catalysts	20 lb/ton of vanadium processed
Consumptive Uses	
Coal	6.9 lb/1,000 tons of coal fired
Oil	51 lb/1,000 bbls of oil fired

SOURCES OF VANADIUM

Vanadium is a grayish malleable, ductile element found combined in many minerals. It melts at 1,900 C and has an atomic weight of 50.942. It is used especially to form alloys.

Vanadium occurs in more than 65 vanadium-bearing minerals and is widely distributed over the world with significant deposits in Peru, South Africa, Russia, and the United States.

Vanadium is found in the minerals patronite, bravoite, sulvanite, davidite, and roscoelite. It also occurs as a secondary element in such uranium-bearing sandstones as carnotite, uravanite, tyuyamunite, and hewettite; in ferrophosphorus derived from domestic phosphate rock; and in titaniferous magnetite ores.

Ores containing vanadium are found in the following states: Alabama, Arizona, Arkansas, Colorado, California, Idaho, Montana, Nevada, New Jersey, New Mexico, New York, North Carolina, Oregon, Rhode Island, South Dakota, Utah, and Wyoming.

The concentration of vanadium in ores varies widely; from less than one percent to as high as 25 percent. In roscoelite,

vanadium pentoxide (V_2O_5) accounts for 20 percent of the total ore but in most of the vanadium-bearing titanium ores, the V_2O_5 content is from 0.1 to 0.3 percent and is removed as an impurity. The phosphate rocks of Idaho and Montana contain from 0.11 to 0.45 percent V_2O_5.

Vanadium is also found in coal and oil. Vanadium compounds are major constituents in some crude oils.

VANADIUM

MATERIAL FLOW CHART - 1968

(Short Tons)

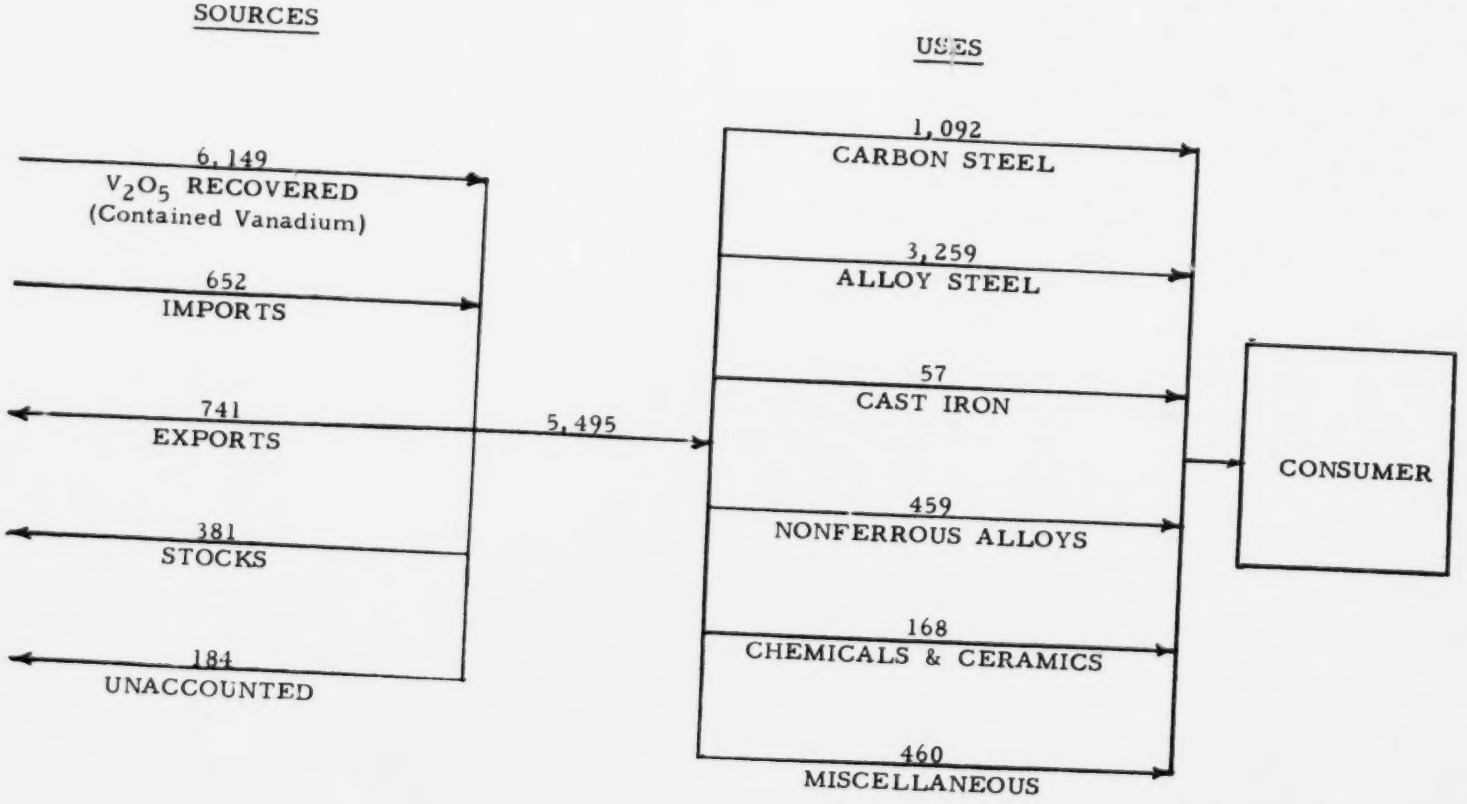

Figure 1

MATERIAL FLOW

MINING AND PROCESSING

During 1968 the recoverable vanadium contained in uranium and vanadium ores and concentrates received at mills, plus vanadium recovered from ferrophosphorus derived from domestic phosphate rock, was 6,483 short tons. Vanadium pentoxide, the most common mill product, amounted to 6,149 short tons (contained vanadium) 1/.

Four mills were in operation recovering vanadium from uranium-vanadium ores in Colorado, Utah, and New Mexico. Two plants in Idaho and Utah extracted it from ferrophosphorus and a new recovery facility at Wilson Springs, Arkansas processed vanadiferous clays 1/.

MINE PRODUCTION OF RECOVERABLE VANADIUM 1/

Location	Contained V Short Tons
Colorado	3,492
Utah	563
Arizona and Other States*	2,428
TOTAL	6,483

*Includes Arkansas, Idaho, New Mexico, North Dakota, Oregon, South Dakota, and Wyoming.

1- Minerals Yearbook: Bureau of Mines; 1968.

IMPORTS AND EXPORTS

During 1968 vanadium imports totaled 652 short tons consisting of ferrovanadium, vanadium ore and concentrate, principally ferrovanadium. Of the 621 short tons (V content) of imported ferrovanadium, approximately 47 percent came from West Germany, 45 percent from Austria, and the remaining 8 percent from Belgium, Luxembourg, France, and Sweden. The 31 short tons (V content) of vanadium ore and concentrate were imported from Canada and the Netherlands Antilles [1].

Exports were 278 short tons (V content) of ferrovanadium and other vanadium alloying materials, and 463 short tons (V content) of vanadium ores, concentrates, oxides, and vanadates. The total exports were 741 short tons [1].

1- Minerals Yearbook; Bureau of Mines; 1968.

VANADIUM STOCKS

Consumer stocks at the end of 1967 amounted to 1,193 short tons of contained vanadium. Producers' stocks as fused oxide, precipitated oxide, vanadiferous slag, metavanadate, metal, alloys, and chemicals totaled 2,231 short tons (V content). The total amount of vanadium stocks was 3,424 short tons [1].

At the end of 1968 consumer stocks were 977 short tons and producers' stocks were 2,828 short tons, totaling 3,805 short tons [1]. Therefore, vanadium stocks increased 381 short tons over the previous year.

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1 - Minerals Yearbook. Bureau of Mines; 1968.

REPROCESSING

The apparent consumption of vanadium in the United States during 1968 has been reported at 5,495 short tons. Of this amount 4,350 short tons, or about 80 percent, were used in making various steels [1].

CARBON STEEL

Ordinary carbon steels depend mainly on their carbon content for their properties and they represent the largest proportion of steel produced. In carbon steels in the United States there are specified minimums and maximums for certain elements, but there is no minimum specified for vanadium. Vanadium is chemically active, easily forming oxides, nitrides, and carbides at elevated temperatures. For this reason vanadium is used in small quantities in the steelmaking process to obtain uniform grain size, and to assist in the removal of oxygen and nitrogen from the melt.

In the United States during 1968 the consumption of vanadium in carbon steel was 1,092 short tons contained vanadium [1]. This represents about 20 percent of the total vanadium consumed during the year.

---

1. Minerals Yearbook; Bureau of Mines; 1968.

ALLOY STEEL

Vanadium is added during the production of some alloy steels in order to control grain size and improve various properties. It will increase the strength at elevated temperatures and the alloy will also be harder, tougher, and more wear resistant. Generally the vanadium content ranges from 0.1 to 0.5 percent but, in some instances, as much as 4 or 5 percent is added.

During 1968 almost half of the vanadium produced in the United States was used in a group of alloys known as high-strength, low-alloy steels. Its purpose is to increase the yield point from the usual 35,000 psi to about 60,000 psi, thus making the steel more desirable for many construction applications such as bridges, towers, and buildings. It is also employed in the manufacture of line pipe for high-pressure gas transmission pipe lines. The nominal vanadium content in high-strength, low-alloy steels is 0.1 percent.

High speed and tool steels are another important group and about 11 percent of the domestic vanadium supply was used for this purpose. Alloys in machine tools for metal removing operations such as cutting, reaming, drilling, and hobbing contain from 1 to 4 percent vanadium. Cold work steels for wrenches,

punches, arbors, shock-resistant pneumatic tooling, accurate gages, and thread rolling dies typically contain 0.2 to 0.3 percent, although one type containing 4.5 percent vanadium is available. Other tool steel alloys are about the same; usually they contain only a small amount of vanadium.

Stainless steel has a great number of commercial and industrial applications due to its corrosion resistance and pleasing appearance. One alloy, type 422 containing 0.3 percent vanadium, can be hardened and tempered to provide a very stable material. This stainless steel contains 12 percent chromium and is used in steam power turbines for blades, rotors, and fasteners; also in jet engine compressor parts. It is less expensive than nickel high-temperature alloys and has some other advantages; however, the operating temperature capability is lower.

In the United States during 1968 the consumption of vanadium in alloy steel was 3,259 short tons (V content); a little less than 60 percent of the total domestic supply [1].

CAST IRON

Vanadium, one of the common alloying elements in cast iron,

1- Minerals Yearbook; Bureau of Mines; 1968.

is generally used in amounts between 0.08 and 0.2 percent in combination with other alloying elements such as chromium, molybdenum, and nickel.

Vanadium increases the tensile strength and hardness of cast iron and in combination with chromium and molybdenum improves heat-treatment hardenability, wear resistance, and higher temperature properties. When used with molybdenum, finer and more uniform graphite flakes result. Vanadium cooperates with chromium, molybdenum, and nickel to decrease the total amount of ingredients needed for a good cast iron alloy.

In 1968 the cast iron industry in the United States used 57 short tons of contained vanadium, or approximately one percent of the total consumption [1].

NONFERROUS ALLOYS

Vanadium is a good stabilizer in titanium and improves hot and cold workability. Thus the titanium alloys can be strengthened by heat treatment. Molybdenum, tantalum, and columbium are also used with titanium, but vanadium has been the most popular due to the following advantages: (1) a lower melting temperature

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1 Minerals Yearbook Bureau of Mines. 1968.

resulting in fewer segregation problems; (2) stronger stabilizing power; (3) lower density, and, (4) cost. Titanium alloys are used in a variety of industries: aerospace, jet engine production, airframes, desalination, and chemical process equipment.

High percentages of aluminum and vanadium occur in certain commercially prepared alloys. The vanadium content is either 2.5, 5, 40, or 85 percent with the remainder in aluminum and fractional percentages of silicon, iron, and oxygen. These alloys are used for control of thermal expansion, grain size, electrical resistivity and improvement of high-temperature strengths.

Alloys based on vanadium are now being used in the nuclear industry as fuel cladding for experimental liquid-metal cooled, fast-breeder reactors. These alloys may replace austenitic stainless steels in this application due to vanadium's nuclear characteristics. It has a higher creep strength and may have a greater resistance to neutron damage than stainless steels.

Vanadium can also be alloyed with columbium and tantalum for use in coatings to withstand high temperatures and for brazing. These alloys are still generally experimental.

In the United States during 1968, 459 short tons of contained vanadium were used in nonferrous alloys; approximately 8 percent of the total vanadium consumption [1].

CHEMICALS AND CERAMICS

Vanadium in the form of inorganic compounds is important as a catalyst in chemical manufacture. The largest use is in the production of sulfuric acid. Vanadium catalysts have a higher efficiency, better immunity to poisoning by arsenic and chlorine, longer life, greater physical ruggedness, and good availability.

Vanadium catalysts are also used in the synthesis of phthalic anhydride from napthalene or ortho-xylene. Phthalic anhydride is the basic raw material used in alkyd, cellulose, and vinyl resins. Alkyd resins are used in manufacturing surface coatings and paints. Cellulose and vinyl resins are used in a wide variety of products. Maleic anhydride, also produced by using a vanadium catalyst, is important in the manufacture of resins and plastics. Adipic acid, a basic raw material in nylon production, employs an ammonium metavanadate catalyst.

A recent development is the use of vanadium pentoxide and

1- Minerals Yearbook; Bureau of Mines; 1968.

aluminum trioxide in afterburners for oxidizing hydrocarbons in automobile exhaust gases. Some vanadium catalysts are also used to accomplish the cracking of petroleum.

Minute quantities of vanadium pentoxide in glass manufacture give hues ranging from almost colorless through various shades of green, yellow, tan, amber, and gray. A few of the vanadates used in coloring glass are cobalt vanadate, manganese vanadate, copper vanadate, and nickel vanadate. Vanadium has been one of the least used elements listed among the fundamental glass coloring agents.

Compounds of vanadium are used in the ceramic industry for glazes and enamels. Vanadium oxide mixed with vanadium salts and zirconia produce a yellow color while other mixtures can result in a blue or red color. Vanadium pentoxide fritted in the proper composition with tin produces a yellow tin-vanadium stain which has largely replaced the uranium yellows.

During 1968 in the United States 168 short tons of contained vanadium, or 3 percent of the total consumption, were used in chemical and ceramic manufacture.

MISCELLANEOUS

Permanent magnetic alloys of iron-cobalt materials with 10 to 15 percent vanadium have been developed. These materials are used in computers where small components need very high field strengths. Some iron-cobalt alloys have excellent magnetic properties but poor electrical resistivity and poor workability. By using 2 percent vanadium in these alloys, they can be used in receiver diaphragms and specialized small power transformers for radar and radio.

Hardfacing is a process of covering a specific area or a whole surface with some composition to accomplish more wear resistance. The process is used where machinery is subjected to abrasive wear, inexpensive tough materials are needed, and lubrication is impossible. Such areas of work include oil well drilling, earth moving, and ore mining.

Hardfacing alloys vary greatly in composition. Vanadium is used in a number of grades with an iron base and is usually present in amounts from 0.5 to 2.5 percent.

Some welding wires have vanadium as a part of their composition. One such wire contains vanadium, nickel, manganese, and molybdenum and is used to weld certain alloy steels.

Another wire containing chromium, molybdenum, and vanadium is used to weld heat-treated, medium-carbon, low-alloy steels. Vanadium in welding wire does not add special properties in the weldment but is added only to match base metal composition.

Some vanadium is used in one of a number of cobalt-chromium alloys that have been developed for tooling applications. These alloys cannot be hot-worked practically so they are used as castings. The alloy used generally contains 38 to 40 percent cobalt, 25 to 32 percent chromium, 10 to 20 percent tungsten, and 2 to 2.5 percent carbon. The alloy containing vanadium uses 3 percent of this element.

Vanadium compounds in paint and varnish promote rapid drying and produce a tough, uniform, smooth film. A group of driers, based on soluble vanadium salts, are fairly strong surface-drying catalysts and are used to a small extent, more particularly in printing inks. Ammonium metavanadate is often used.

Vanadium chloride has been used in photographic processes for toning silver bromide prints to impart a green color.

Compounds of vanadium have been used as antiseptics; inhibitors of germ and organism growth; to treat abscesses, infected wounds, sores, and ulcers; destroyers of fermentation

microbes; to treat anemia; boost appetite and improve nutrition. A University of Kansas Medical School research team advances the theory that vanadium salts tend to reduce deposits and discourage production of cholesterol.

Small amounts of vanadium pentoxide are used in textile printing to give black dyes greater intensity and fastness.

Miscellaneous use of vanadium in the United States during 1968 amounted to 460 short tons contained vanadium. This is about 8 percent of the total consumption.

EMISSIONS

MINING AND PROCESSING

Prior to 1948, Colorado uranium-vanadium ores were mined underground at a shallow depth on a highly selective basis. The operation was usually on a small scale and there was little mechanization. However, since that time the emphasis has shifted to uranium recovery and mining methods have changed. Vertical shafts as deep as 600 feet are currently used to reach deposits in the Colorado Plateau.

Many of the mines are small and mining methods vary. However, drilling and blasting are usually required to loosen the ore before it is loaded on a conveyance for transport to the surface. Next comes another loading operation as the ore is transferred to trucks for the journey to the mill.

Since there is a low vanadium content in surface-mined ores from the Colorado Plateau, there has been little open-pit mining. However, where surface mining is used the overburden is loosened with explosives and then removed. Ore is then loaded into trucks or train cars for the trip to the mill. This same type of operation is employed in open-pit mines in New Mexico and Arkansas.

In the most widely used vanadium extraction processes, the ores are put through dry grinding, mixed with lime and salt, and roasted. The resulting product from the roaster, sodium vanadate, is leached with water, acid, or a basic solution. The vanadium is precipitated from this solution in a form known as "red cake", a sodium polyvanadate. By redissolving the "red cake" ammonium metavanadate is precipitated, which is then fused to yield vanadium pentoxide. This technical-grade vanadium pentoxide contains a minimum of 86 percent vanadium pentoxide and 6 to 10 percent sodium oxide.

While this study was in progress several of the larger companies were contacted concerning mining and processing methods, as well as vanadium emissions to the atmosphere. Records of vanadium emissions were not available, but estimates obtained indicated average atmospheric emissions are about 25 pounds per ton of vanadium handled.

Vanadium emissions to the atmosphere during 1968 from sources of mining and processing totaled 81 short tons. This estimate includes emissions during the production of vanadium pentoxide.

METALLURGICAL PROCESSING

During 1968 nearly all of the vanadium produced in the United States was recovered as vanadium pentoxide (V_2O_5), which was further processed into ferrovanadium for use principally by the steel industry. The vanadium consumption was 5,495 tons, including 4,712 tons in the form of ferrovanadium. The vanadium used as an alloy in steel was 4,350 tons.

Ferrovanadium is produced by the reduction of vanadium ore, slag, or a technical-grade oxide with carbon, ferrosilicon, or aluminum. Carbon is a cheaper raw material for reducing vanadium, but there is a problem with carbon control in the finished product. Electric reduction furnaces are used for smelting ores to produce ferrovanadium. Furnace production is continuous with charges placed in the furnace at the top and the molten product tapped near the bottom.

Low carbon grades of ferrovanadium are produced by reducing technical-grade vanadium pentoxide with ferrosilicon. Since silicon is not a powerful reducer of vanadium oxides, a two-step process is required. A charge of 90 percent grade ferrosilicon, lime, vanadium pentoxide, and some fluorspar is smelted in an electric furnace lined with magnesite. This yields an iron alloy

containing about 30 percent vanadium, but undesirable amounts of silicon. In the second step the silicon is decreased by adding more vanadium pentoxide and lime so that most of the silicon goes into the slag phase. This slag contains some vanadium and is returned to the first step for vanadium recovery.

The preparation of ferrovanadium using a silicon process is being used commercially to produce tonnage quantities. A reaction between vanadium-bearing slags, silica, flux, and a carbonaceous reducer takes place in a submerged-arc electric furnace to produce a vanadium silicide alloy. This alloy is refined with vanadium oxide so that the alloy contains less than 20 percent silicon. This is then reacted with a molten vanadiferous slag in the presence of lime. This produces a ferrovanadium alloy called Solvan of approximately 28 percent vanadium, 11 percent other metals, and the remainder iron.

Aluminum is a more expensive reducing agent; however, the product is relatively pure and the recovery of vanadium is high. A charge of technical-grade vanadium oxide, aluminum, iron scrap, and a flux is put into an electric arc furnace. Since this is an exothermic reaction, no carbon is required in the charge. The reaction between the vanadium pentoxide and aluminum is

initiated by the arc. Ferrovanadium containing as much as 80 percent vanadium is produced in this manner.

Another process is the thermite reaction in which vanadium and iron oxides are both reduced by aluminum granules in a magnesite lined steel vessel or a copper crucible cooled by water. The reaction is produced by a barium peroxide-aluminum ignition charge.

In each of these methods the vanadium pentoxide is melted before it is used in alloying. During this melting process, there is a vapor of the pentoxide produced that becomes an aerosol. Then during the actual reduction process in the furnaces, the vanadium pentoxide goes to tetroxide, trioxide, oxide, and finally vanadium metal.

In addition to its use in the production of ferrovanadium, vanadium pentoxide is reduced with calcium to produce vanadium metal of about 99.5 percent purity. An exothermic reaction is carried out in a sealed vessel and it is initiated either by preheating the vessel or internal heating with a fuse wire embedded in the charge. Iodine has been added to the calcium and vanadium pentoxide charge. Calcium iodide is produced by the reaction and serves as both a flux and thermal booster. Two

problems with this process are that metal yields amount to only 75 to 80 percent, and there is a high amount of calcium required.

Most of the vanadium metal of 99 percent purity used for alloying purposes is produced commercially by the alumino-thermic process. In this process vanadium pentoxide in powder form is reacted with high-purity aluminum in a "bomb", or sealed vessel, to form a vanadium-aluminum alloy. The reaction is initiated by a vanadium fuse wire. A molten alloy of vanadium and aluminum separates from a fused aluminum oxide slag and settles to the bottom of the vessel. The vanadium alloy is then purified by crushing the brittle alloy and heating plus electron beam melting, or two steps of direct electron beam melting of the vanadium-aluminum alloy.

Vanadium can be even further purified by one of three methods: iodide refining, electrolytic refining in a fused salt, or electrotransport. In iodide refining an impure grade of vanadium metal is reacted with iodine at 800 to 900 C to form vanadium diodide in volatilized form which is thermally decomposed and deposited on a hot filament. This process is carried out in an evacuated and sealed tube. The electrolytic refining process involves the cathodic deposition of vanadium from an electrolyte in solution.

Electrotransport has been reported as producing the highest purity vanadium. A high-density current is passed through a rod of electrolytically refined metal, heating it to 1,700 to 1,850 C. Atoms of carbon, oxygen, and nitrogen migrate to the negative end of the bar, resulting in a high degree of purification along the remainder of the bar.

Vanadium carbide is a product which may be used as a replacement for ferrovanadium in steel making, and there are two methods of manufacturing. In one method a powdered vanadium metal, or hydride and carbon, is heated in a vacuum furnace as high as 2,000 C without an excessive loss of vanadium. When a low carbon content product is needed, low temperatures must be used or there will be an excessive loss of vanadium to oxygen.

Vanadium emissions to the atmosphere from electric furnaces producing ferrovanadium have been determined to be 49 pounds per ton of vanadium processed. The particle size generally ranges from 0.1 to 1 micron and the total particulate emission is 240 pounds per ton of charge [1]. This data is based on uncontrolled emissions, stack samples, and chemical analysis of the particulate matter.

1- Private communication with industrial source.

In addition to furnace operations, other emissions occur during materials handling. These emissions are estimated at 12 pounds per ton of vanadium.

In the United States during 1968 vanadium emissions to the atmosphere resulting from the production of ferrovanadium totaled 144 short tons.

REPROCESSING

Vanadium is an important alloying element in steelmaking. It is used in the form of ferrovanadium in relatively small quantities and is usually added to the melt near the end of the refining period or after the steel is in the ladle.

From the standpoint of air pollution, the vanadium added to the melt is not as important as the vanadium that is contained in the raw materials, the steel scrap and the iron ore.

Certain types of iron ore contain vanadium from a trace to more than one percent V_2O_5. In titaniferous magnetites, the content ranges from about 0.2 to more than one percent and probably averages about 0.5 percent. In nontitaniferous magnetites vanadium is reported in only a few of the deposits, and these contain 0.1 to about 0.3 percent V_2O_5 [1].

In some instances vanadium has been recovered from iron ore. During World War II this source was taken up actively in Germany. The iron ore was melted in the blast furnace in the normal manner, 80 to 90 percent of the vanadium remaining with

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1- Busch, P. M.; "Vanadium - A Materials Survey"; U. S. Bureau of Mines; Information Circular 8060; p. 27; 1961.

the pig iron. On transferring to an acid-lined Bessemer converter and blowing for 3 to 5 minutes, 80 percent of the vanadium was recovered in the slag as vanadium pentoxide [1].

During this study information was obtained from several industrial sources regarding the vanadium content of iron ore processed in the United States. Actual data was not available and estimates varied considerably; however, all agreed the average would not be more than 0.1 percent and likely not less than 0.01 percent. In this report an average figure used is 0.03 percent.

STEEL

The basic steps in the production of steel include the partial removal of impurities when the iron ore is reduced to pig iron in the blast furnace. Further purification takes place as pig iron and scrap are converted to steel in an open-hearth, a basic oxygen, or an electric furnace. Other associated operations include ore crushing, materials handling, sintering, pelletizing and scarfing.

Blast Furnace - The blast furnace is a large refractory lined vessel into which iron ore, coke, and limestone are charged and

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1- Dennis, W. M.; Metallurgy of the Nonferrous Metals; Sir Issac Pitman and Sons, Ltd.; London; 1961.

reacted with large amounts of hot air to produce molten iron. Slag and blast furnace gases are byproducts from this reaction. As the gas leaves the top of the furnace it contains large quantities of particulates averaging about 150 pounds per ton of pig iron [1]; however, it is subsequently cleaned and used as fuel. The gas cleaning is usually accomplished in three stages and the annual overall efficiency of cleaning is estimated at 97 percent.

During 1968, 140 million tons of net ores and agglomerates were consumed in producing 89 million tons of pig iron [2]. The estimated vanadium content of the ore was 0.03 percent and the vanadium leaving the blast furnace was about 5 percent of the amount contained in the charge. Vanadium emissions to the atmosphere during the year were 1.4 pounds per thousand tons of pig iron produced; a total of 63 tons.

Open-Hearth Furnace - Three types of furnaces are commonly used in steelmaking: the open-hearth, the basic oxygen, and the electric furnace. In all instances, regardless of the type of furnace, the primary object of the operation is to reduce the

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1- "Air Pollutant Emission Factors"; Environmental Protection Agency; Preliminary Document; April 1971.

2- Minerals Yearbook; Bureau of Mines; 1968.

impurities present in the charge to the limits specified for the different melts. In the open-hearth furnace, steel is made from a mixture of scrap (about 45 percent) and pig iron (about 55 percent) in a shallow basin or hearth. Oil, coke-oven gas, natural gas, tar, or producer gas provides the required heat.

The open-hearth process consists of several steps or stages:

Tap to start	Ore and lime boil
Charging	Working
Meltdown	Tapping
Hot-metal addition	Delay

The melting step begins when the first scrap has been charged and continues as the solid material is added. After the charge has melted, molten pig iron is delivered and poured into the furnace. The next step is the ore and lime boil, which is a bubbling action caused by the oxidized gases rising to the surface. The purpose of the working period is to: (1) lower the phosphorus and sulfur content; (2) eliminate carbon as rapidly as possible; and (3) increase the heat for final deoxidation or for tapping. At the end of the working period the temperature of the melt is approximately 3;000 F.

The overall operating cycle of the open-hearth furnace is about ten hours and fumes or metal oxides are discharged continuously at varying rates. In spite of the variations, average emission

factors have been established for operation both with and without oxygen lancing. With oxygen lancing, the factor for uncontrolled emissions is 21 pounds of particulate per ton of steel; without lancing, the factor is 8 pounds per ton. The degree of emission control is estimated at 40 percent, and the average emission factor (controlled) for all open-hearth furnace operations is 10.2 pounds of particulate per ton of steel produced [1].

During 1968 the steel produced in open-hearth furnaces was 65 million short tons [2] and the vanadium content of the particulate matter emitted was about 0.05 percent [3]. Vanadium emissions to the atmosphere were 5.1 pounds per thousand tons of steel produced; a total of 166 tons.

Basic Oxygen Furnace - The basic oxygen furnace, in many respects, is similar to the well known Bessemer converter. The principal difference is in the means for supplying oxygen to the molten metal. The converter is a refractory-lined, cylindrical

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1- "Emissions, Effluents, and Control Practices"; Environmental Protection Agency; Study in progress (unpublished); 1970.

2- Minerals Yearbook; Bureau of Mines; 1968.

3- "Air Pollution Engineering Manual"; Public Health Service Publication No. 999-AP-40; p. 243; 1967.

vessel mounted on trunions. It can be rotated to a horizontal or a vertical position as required during operation. When charged and in the vertical position, a stream of oxygen is supplied from overhead downward into the converter. The oxygen impinges on the liquid metal surface causing violent agitation and intimate mixing with the pig iron. The overall operating cycle is about one hour.

The emission factor for the basic oxygen furnace has been estimated at 46 pounds of particulate per ton of steel [1] and the degree of emission control at 97 percent.

During 1968 the steel produced in basic oxygen furnaces was 48 million short tons [2] and the estimated vanadium content of the particulate emissions was 0.02 percent. Vanadium emissions to the atmosphere were 0.3 pound per thousand tons of steel produced; a total of 7 tons during the year.

Electric Furnace - Electric arc furnaces are well suited to the production of alloy steels and are used extensively for that purpose. They are refractory-lined, cylindrical vessels with

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1- "Air Pollution Emission Factors"; Environmental Protection Agency; Preliminary Document; April 1971.

2- Minerals Yearbook; Bureau of Mines; 1968.

large carbon electrodes passing through the furnace roof.

Emissions generated during steelmaking consist of fume and dust emitted from the furnace during charging and refining. While charging the furnace, the top is open to receive the cold metal and the exposure of the cold charge to the high temperature inside the furnace results in the generation of large quantities of fume. In general, the rate of fume release increases throughout the operation reaching a peak as the pour temperature is approached.

Particulate emissions from electric arc furnaces have been estimated at 11 pounds per ton of steel with oxygen lancing, and 7 pounds per ton without [1]. The degree of control is estimated at 78 percent, and the average emission factor (controlled) at 2.5 pounds per ton of steel produced.

During 1968 the steel produced in electric arc furnaces was 16 million short tons [2], and the estimated vanadium content of the particulate emissions was 0.003 percent. Vanadium emissions to the atmosphere during the year were negligible; less

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1- "Air Pollution Emission Factors"; Environmental Protection Agency; Preliminary Document; April 1971.

2- Minerals Yearbook; Bureau of Mines; 1968.

than one ton.

CAST IRON

During this study spectrographic analyses of dust samples from foundries have been examined; they all indicated vanadium and many other elements are contained in the dust.

The cupola is the most used method for producing cast iron. The rate of particulate emissions from gray iron cupolas has been reported as 4 to 26 pounds per ton of process weight not including emissions from handling, charging, or other non-melting operations.

Based on the information obtained from industry the particulate emission factor is estimated at 22 pounds per ton of process weight, including melting and non-melting operations. The vanadium content of the particulate is about 0.001 percent [1]/ and the degree of emission control approximately 25 percent.

During 1968 the pig iron and scrap used by iron foundries totaled 16,788,000 short tons [2]/. Vanadium emissions to the

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1- Private communication with industrial source.

2- Minerals Yearbook; Bureau of Mines; 1968.

atmosphere due to the production of cast iron were one ton.

NONFERROUS ALLOYS

Vanadium is employed as an alloying agent to control grain size, thermal expansion, and electrical resistivity and to improve high temperature strength. It is used mostly with aluminum and titanium; production methods are generally the same as those used with other alloys.

Based on information obtained from two industrial sources, vanadium emissions to the atmosphere are estimated at 12 pounds per ton of vanadium processed. During 1968 the emissions were 3 tons.

CHEMICALS AND CERAMICS

Catalysts - Compounds of vanadium are important to the chemical industry as catalysts for many industrial processes including the synthesis of sulfuric acid, the oxidation of hydrocarbons, and the polymerization of mono- and di-olefins. However, the quantity used by the chemical and related industries is small compared with metallurgical applications.

Catalyst manufacturers use either ammonium metavanadate or vanadium pentoxide as a starting material. In one process

vanadic acid is produced first, then caustic potash, dilute sulfuric acid, and water are added; they are all mixed to damp earth consistency. The mass is then dumped on a drying band heated by exit gases from the calcining furnace. The band goes into the furnace for about 25 minutes at 800 C. Upon exit, the dried granules are cooled and sieved. Sieve residue is ground and used again.

Manufacturers of catalysts contacted during this study stated their atmospheric emissions are about 20 pounds of vanadium per ton of vanadium processed. During 1968 vanadium emissions to the atmosphere resulting from the manufacture of catalysts totaled 2 tons.

Glass and Ceramics - The use of vanadium in glass and ceramics is limited and shows little promise of potential growth. About 2 tons per year are consumed in the production of a yellow stain for coloring pottery and glass.

The main steps in glassmaking are: (1) compounding the mixtures or "charge"; (2) heating in a fire-clay pot to about 2,800 F; (3) heat purification or cooking; (4) shaping the glass objects by blowing, pressing, or casting; and, (5) gradual cooling in an oven.

In the manufacture of glazes the dry ingredients are usually mixed in the presence of an excess of water although it may be desirable to mix them dry. Glaze materials are measured dry before pouring into a mixer. After thorough mixing, there is a grinding stage generally with a ball mill.

Dry mixing is usually done with a frit batch. Measuring, pouring, mixing, and grinding are carried on in a way very similar to wet mixing. There is, however, one additional step; the dry mixture goes through a crushing stage. This is to keep the batch from clogging the ball mill.

Emissions due to making glass and ceramics were negligible.

MISCELLANEOUS

Permanent magnetic alloys consist of iron, cobalt, and about 15 percent vanadium. They are made in a manner similar to cast iron and vanadium is added in the ladle before pouring into molds.

Welding rods and wires are usually made from steel produced in an open-hearth furnace. Any vanadium used in these products is added to the steel in the ladle. The steel billets are heated and formed into rods in the rolling mill. These rods are then drawn into wire.

Compounds of certain metals soluble in paint oils are used as driers. They may be prepared separately and added in the damp paint mixing process, or they may be an incorporated part of the paint oil through chemical reaction. Liquid paint drier is prepared especially for addition to paint. Driers may be added to varnishes during the cooking period or later. Varnish cooking temperatures usually vary from 450 to 600 F.

A vanadium compound, vanadium chloride, is used for toning silver bromide in the development of color film. This development process involving vanadium occurs in solution. The vanadium chloride used is made first by heating vanadium pentoxide with sulfur monochloride to produce vanadium trichloride. Disproportionation of the trichloride at 800 C in a stream of nitrogen produces vanadium chloride.

Information obtained during this study varies considerably regarding vanadium emissions from reprocessing operations. Estimates have ranged from less than 0.25 to 5 percent. Average emissions are estimated at 10 pounds per ton of vanadium processed.

During 1968 vanadium used in miscellaneous reprocessing operations totaled 460 tons, and atmospheric emissions were 2 tons.

CONSUMPTIVE USES

The largest vanadium emissions to the atmosphere are those that are due to the combustion of coal and oil. Those that occur during other consumptive uses are mostly of such a nature that atmospheric emissions are negligible.

COAL

During the combustion of coal vanadium is discharged with the ash; part with the bottom ash and part with the fly ash. On the average about 65 percent of the total ash is fly ash.

With respect to fly ash, a study has been made regarding emissions from coal fired power plants and the emissions of vanadium have been recorded. Six power boilers were tested, each a different type, and each value reported was the average of at least two tests. Two of the boilers were fired with Illinois coal; two burned Pennsylvania coal; one used some coal from Ohio and some from West Virginia; one burned part Kentucky and part West Virginia coal. The coal burned during the tests represented only a small portion of the coal mined in the various regions of the United States. Vanadium concentrations in the fly ash samples taken after fly ash collection ranged from 0.88 to 6.6 grains per

scf x 10^{-4} [1]. The average was 2.91 grains per scf x 10^{-4}. Based on 508,990,000 tons of coal consumed in the United States during 1968 [2], 90 percent application of control, a vanadium concentration of 2.91 grains per scf x 10^{-4}, and 160 scf of flue gas per pound of coal, the vanadium emissions due to the combustion of coal are calculated at 3,760 tons.

$$\frac{508,990,000 \times 160 \times 2.91 \times 10^{-4} \times 2,000}{7,000 \times 2,000 \times 0.9} = 3,760$$

Many samples of coal have been analyzed and the vanadium content reported is shown in Table I. Based on a vanadium concentration in coal averaging 22.5 ppm, 90 percent application of control and 85 percent efficiency of control, the vanadium emissions calculated in this manner totaled 1,750 tons.

$$508,990,000 \times 22.5 \times 10^{-6} \times 0.65 \left[1 - (0.85 \times 0.90)\right] = 1,750$$

In this report the figure of 1,750 tons is used as the vanadium emissions to the atmosphere during 1968 due to the combustion of coal.

1- Cuffe, Stanley T. and Gerstle, Richard W.; "Emissions from Coal Fired Power Plants"; Public Health Service Publication No. 999-AP-35; 1967.

2- Minerals Yearbook; Bureau of Mines; 1968.

TABLE I

AVERAGE MINOR ELEMENT CONTENTS OF COALS FROM VARIOUS REGIONS OF THE UNITED STATES - PPM

Region	Ash Content of Coal - %	V Content of Coal - ppm
Northern Great Plains	13.42	16.0
Eastern Interior	6.16	35.0
Appalachian	6.11	21.0
Western and Southwestern	NR*	18.0
Average Vanadium Content in Coal		22.5

*Not reported

NOTE - The above table based on Geological Survey Bulletins 1117-C and 1117-D.

OIL

In order to estimate vanadium emissions to the atmosphere due to the combustion of fuel oil, it was necessary to determine the vanadium content, as well as the quantity, of oil received from numerous foreign and domestic sources. Analyses of more than 400 samples of crude and residual oils were obtained from the major oil companies and the utilities along the east coast of the United States.

The data show that nearly all crude oil contains some vanadium; the concentrations ranging from nearly zero to more than 1,000 ppm. It also shows that residual oil contains a higher percentage of vanadium than the crude. When oil is refined the vanadium and other trace metals tend to concentrate in the heavy fractions; the residual oil, the road oil, and the asphalt. According to the information obtained from oil companies, the residual fuel oils may be expected to contain 30 to 90 percent more vanadium than the crude oils.

Unfortunately, most of the analyses available were of crude oil. They show oil from California contains more vanadium than that from Kansas, Oklahoma, and Texas (Table II). Crude from western Venezuela has a much higher concentration than crude from the eastern part of the country (Table III) or that from

TABLE II

VANADIUM CONTENT OF DOMESTIC CRUDE OILS

Source	Vanadium Content - ppm
Arkansas	9.3
California	50.0
Colorado	0.44
Kansas	15.1
Louisiana	0.5
Montana	78.0
New Mexico	0.1
Oklahoma	4.0
Texas	2.6
Utah	4.6
Wyoming	49.7

NOTE - The above table is based on private communication with industrial sources.

TABLE III

VANADIUM CONTENT OF VENEZUELAN CRUDE OILS

Crude	Gravity API	Vanadium Content - ppm
Western Venezuela		
Bachaquero Heavy	13.2	390
Bachaquero	16.6	370
Bachaquero Light	35.4	49
Barinas	25.9	165
Boscan	10.6	1,400
Cumarebo	47.8	0.7
Lagunillas Heavy	17.6	300
La Rosa Medium	23.9	230
Mara	29.5	220
Mototan #7	19.7	390
Taparito	17.2	450
Tia Juana Light	31.9	100
Tia Juana Medium	25.6	200
Tia Juana Heavy	18.2	300
Urdaneta	11.3	430
Eastern Venezuela		
Cachipo	34.3	14
Guanipa	32.7	110
Jusepin	31.9	26
Oficina Light	35.3	57
Oficina Heavy	31.5	62
Pedernales	21.7	230
Pilon	9.7	510
Quiriquire	16.5	95
San Joaquin	45.9	0.6
Temblador	20.6	56
Tigre	26.5	160
Tucupita	15.7	84

NOTE - The above table is based on private communication with industrial sources.

other foreign sources (Table IV). Residual oil from South America contains about 280 ppm vanadium; from the Middle East about 50 ppm; and from the United States 30 ppm.

During 1968 the demand for residual fuel oil in the United States was 668,239,000 barrels. Imports were 409,928,000 barrels, and the remainder were principally from domestic production 1/. Imports were about 92 percent from South America and the West Indies; 8 percent from the Middle East, Canada, and other countries 2/.

VANADIUM IN RESIDUAL OIL
CONSUMED IN THE UNITED STATES - 1968

Source	Quantity Barrels	V Content ppm	V Content Tons
United States	258,311,000	30	1,280
South America	376,000,000	280	17,350
Middle East and Other	33,928,000	50	280
TOTAL	668,239,000		18,910

1- "Crude Petroleum, Petroleum Products, and Natural-Gas-Liquids: 1968"; Petroleum Statement, Annual; Mineral Industry Surveys; Bureau of Mines; Washington, D. C.

2- Based on import data from the Office of Air Programs; Durham, N. C.

TABLE IV

VANADIUM CONTENT OF MIDDLE EAST CRUDE OILS

Crude	Gravity API	Vanadium Content - ppm
Agha Jari (Iranian)	33.9	36
Ain Dar (Arabian)	33.9	51
Ain Zalah (Iraqi)	32.1	95
Bai Hassan (Iraqi)	33.3	19
Gach Saran (Iranian)	31.0	114
Jambur (Iraqi)	39.2	6
Kirkuk (Iraqi)	36.3	30
Kuwait	32.3	30
Qatar	42.2	3
Safaniya (Arabian)	27.1	80
Shedgum (Arabian)	34.3	18
Uthmaniyah (Arabian)	30.0	51
Wafra (Neutral Zone)	24.1	52
Zubair (Iraqi)	36.4	20

NOTE - The above table is based on private communication with industrial sources.

In the past power boilers designed to burn fuel oil were not usually equipped with air pollution control apparatus. It was only the coal fired or the combination coal-oil units that included mechanical collectors and/or electrostatic precipitators. When these combination units burn oil, only a small part of the particulate matter becomes an atmospheric emission.

The records show that 669 million barrels of residual oil were consumed in the United States during 1968. The electric utilities used 28 percent of the total, or 185 million barrels, and were the only users with any significant degree of air pollution control. A survey was conducted and it was determined that the electric utility percent of control when burning fuel oil was about 32 percent.

Based on 10 percent overall control, the vanadium emissions to the atmosphere during 1968 due to the combustion of fuel oil totaled 17,000 tons.

APPENDIX A

COMPANIES DEALING IN VANADIUM AND VANADIUM PRODUCTS

ALABAMA	LOCATION
S. Bornstein Metals, Inc.	Birmingham
CALIFORNIA	
Centrifugal Products, Inc.	Long Beach
Electronic Space Products, Inc.	Los Angeles
Fred H. Lenway and Company, Inc.	San Francisco
Reactor Experiments, Inc.	San Carlos
Research Inorganic Chemical Corp.	Sun Valley
Rolla Sitkin Metals, Inc.	Los Angeles
COLORADO	
Climax Uranium Company	Grand Junction
ILLINOIS	
L. H. Hedger and Sons Metal Co.	Collinsville
Steel Sales Corporation	Chicago
INDIANA	
Mefco, A Teledyne Company	Elkhart
Union Carbide Corporation	Kokomo
MARYLAND	
Chicago Development Corporation	Riverdale
Max Zuckerman and Sons, Inc.	Owing Mills

MASSACHUSETTS

Benton Corporation	Beverly
Whittaker Corporation	West Concord

MICHIGAN

Frankel Company, Inc.	Detroit
Wolverine Metal Company	Detroit

MISSOURI

Metal Goods Corporation	St. Louis
Whitehead Metals, Inc.	St. Louis

NEW JERSEY

J. T. Baker Chemical Company	Phillipsburg
Hyperrefiners, Inc.	Clifton
M & R Refractory Metals, Inc.	Springfield
E. L. Payer Company	Wenoah
Schiavone-Bonomo Corporation	Jersey City
Shieldalloy Corporation	Newfield
Var-Lac-Oid Chemical Company	Elizabeth

NEW YORK

Advanced Alloys, Inc.	College Point
Alloychem, Inc.	New York City
American Metal Climax, Inc.	New York City
American Nickel Alloy Manufacturing Corporation	New York City
Anglo-American Metal & Ferro Alloy Corporation	New York City
Associated Metals and Minerals Corp.	New York City
Atomergic Chemetals Company	Carle Place, L. I.
Baird Chemical Industries, Inc.	New York City
Belmont Smelting & Refining Works, Inc.	Brooklyn
Paul Blum Company	Buffalo
Brandeis, Goldschmidt and Company	New York City

City Chemical Corporation	New York City
Cometals, Inc.	New York City
Continental Ore Corporation	New York City
Diesel Chemical & Metal Company, Inc.	Brooklyn
Duro-Dyne Corporation	Farmingdale, L. I.
Elgen Manufacturing Corporation	Long Island City
Henning Bros. & Smith, Inc.	Brooklyn
Kolon Trading Company, Inc.	New York City
Materials Research Corporation	Orangeburg
Mercer Alloys Corporation	New York City
Metal Trading, Inc.	New York City
Morgan Chemicals, Inc.	Buffalo
Niagara Falls Metals & Minerals, Inc.	Buffalo
Overseas Metal and Ore Corporation	New York City
Pancoast International Corporation	New York City
Philipp Brothers	New York City
Progressive Alloys Corporation	Brooklyn
Samincorp	New York City
J. A. Samuel & Company, Inc.	New York City
Skandia Metals Corporation	New York City
Stalco International	New York City
Stevens Metallurgical Corporation	New York City
C. Tennant Sons and Company	New York City
Union Carbide Corporation	New York City
United Mineral and Chemical Corp.	New York City
Vanadium Corporation of America	New York City
Samuel J. Zuckerman, Inc.	Floral Park

OHIO

Cleveland-Cliffs Iron Company	Cleveland
Metal Powder Products, Inc.	Logan

OREGON

Oregon Metallurgical Corporation	Albany

PENNSYLVANIA

Bram Metallurgical-Chemical Company	Philadelphia
Chemalloy Company, Inc.	Philadelphia

Derby and Company, Inc.	Pittsburgh
Foote Mineral Company	Exton
Mercer Alloys Corporation	Greenville
Reading Alloys, Inc.	Robesonia
Semi-Elements, Inc.	Saxonburg
Joseph Tyson and Company	Cheltenham
Vitro Manufacturing Company	Pittsburgh

TEXAS

Lloyd M. Parkans Company	Houston
Robinson Orifice Fittings Company	Houston

WASHINGTON

Stoker Engineering Company	Tacoma

(American Metals Market, Jan. 13, 1970; Thomas Register, Dec. 1968 Ed.)

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